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Facile, mild and efficient synthesis of azines using phosphonic dihydrazide

Rizk E. Khidre^{a,b}, Hanan A. Mohamed^{c,d}, Benson M. Kariuki^e, and Gamal A. El-Hiti^f 

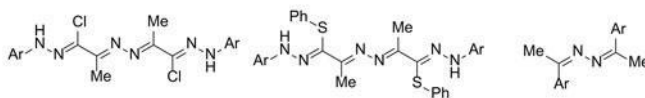
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ABSTRACT

Several bis(N'-arylpropanehydrazonoyl chlorides) were synthesized in good yields from condensation reactions of hydrazonoyl chlorides and phosphonic dihydrazide. Under the conditions employed, none of the expected phosphorylhydrazines were isolated. Nucleophilic substitution of bis(N'-arylpropanehydrazonoyl chlorides) with thiophenol, sodium phenylsulfinate, hydroxyl amine, and piperidine afforded the corresponding azines. Similarly, 1,2-bis(heteroaryl)ethyldene)hydrazines were produced from reaction of phosphonic dihydrazide and heteroaryl methyl ketones. The structures of the products were confirmed by NMR and IR spectral data along with X-ray crystal structure determination and their purities were confirmed by the elemental analyses.

KEYWORDS Phosphonic dihydrazide; azines; nucleophilic substitution reaction; heterocycles; bis(N'-arylpropanehydrazonoyl chlorides); X-ray crystallography

GRAPHICAL ABSTRACT



Introduction

Azines or 2,3-diaza-1,3-butadienes, ($R_2C \frac{1}{4} N-N \frac{1}{4} CR_2$), are important compounds in various synthetic transformations.^[1–4] They have unique chemical structures compared to simple 1,3-butadienes and therefore can produce five-membered heterocycles via 1,3-dipolar cycloadditions.^[5–8]

For example, one-pot reaction of azines and benzylidenemalononitriles, via copper-catalyzed tandem cyclization, gave 1,2,4-triazolo[1,5-a]pyridines.^[9] Azines exhibit various pharmacological activities^[10] and act as antitumor,^[11] anti-convulsant,^[12] antioxidant,^[13] and antimicrobial agents.^[14] In addition, they have interesting industrial applications and can be used as optical materials,^[15] conductive media,^[16] organic sensors,^[17] and semiconductors.^[18]

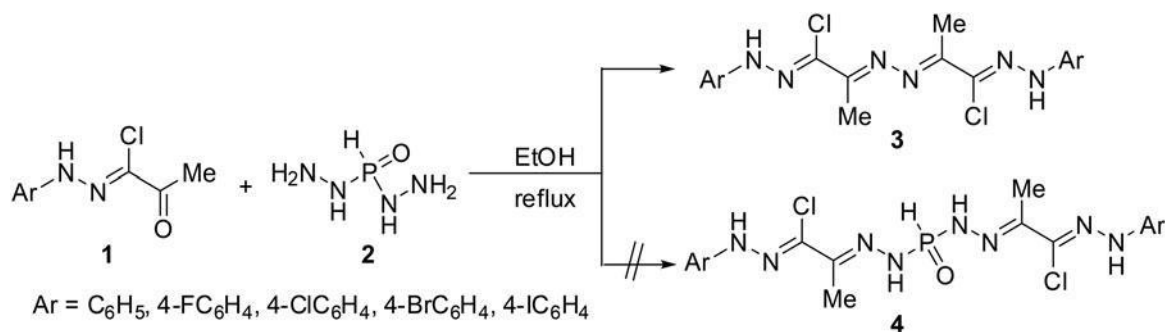
The synthesis of azines involves the condensation reaction of carbonyl compounds and hydrazines such as hydrazine hydrate, hydrazine sulfate or hydrazinium carboxylate.^[19] Also, they can be synthesized from the copper-catalyzed dimerization of imines,^[20] and homo-coupling of ketoximes.^[21] In addition, azines can be directly synthesized from reaction of alcohols and hydrazine hydrate in the presence of ruthenium^[22] or nickel complexes.^[23] Recently, the reaction of 3-hydrazonobutan-2-one oxime and aromatic aldehydes has been reported to produce the corresponding

1,2-bis(arylidene)hydrazines in high yields.^[24] In the current work, a novel series of azines was produced by simple and efficient synthetic procedures from phosphonic dihydrazide, as part of our research program on the synthesis of novel heterocycles.^[25–29]

Results and discussion

Condensation of a 2:1 mixture of 2-oxo-N'-arylpropanehydrazonoyl chlorides **1** and phosphonic dihydrazide (**2**) in boiling ethanol for 3 h gave bis(N'-arylpropanehydrazonoyl chlorides) **3** in good yields rather than the expected products, (2,2'-phosphoryl)bis(hydrazin-2-yl-1-ylidene))bis(N'-arylpropanehydrazonoyl chlorides) **4** (Scheme 1). The ¹H NMR spectra of **3** showed exchangeable singlets that resonated within the 10.32–10.47 ppm region corresponding to the NH protons. The ¹³C NMR spectra of **3** showed all the expected carbons. Moreover, IR and ¹³C NMR spectra of **3** indicated the absence of a carbonyl group. The X-ray crystal structures of **3c** and **3d** are shown in Figures 1 and 2, respectively.

No evidence was found to prove that products **4** were formed under the condition attempted. When an equimolar reaction of **1** and **2** was attempted, only products **3** were



Scheme 1. Synthesis of azines 3.

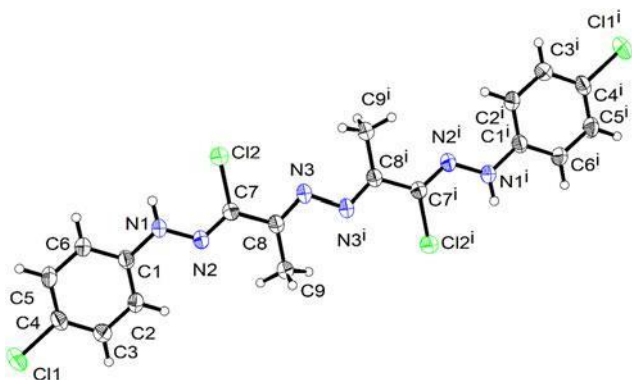


Figure 1. Ortep representation of the molecular structure of 3c showing 50% probability ellipsoids.

produced in low yields along with 1. Such results are not in agreement with the reported ones.^[30,31] Two reports, by the same author(s), showed that reactions of a 2:1 mixture of compounds of the type of 1 and 2 in EtOH for 1–4 h, in the presence or absence of sulfuric acid, gave 4 in 46–91% yields.^[30,31] However, an early report that investigated the reactions between carbonyl compounds and dihydrazides of phosphonothioic acid showed that products either of the type 3 or 4 or a mixture of both could be produced based on the substituents attached to the carbonyl group.^[32] For example, the reaction of 4-methylbenzaldehyde with the dihydrazide of phosphonothioic acid gave the corresponding product of type 3 as the only product in 78% yield.^[32] A proposed mechanism for the formation of 3 from reaction of 1 (two mole equivalents) and 2 is shown in Scheme 2. Based on an early report,^[32] it is believed that the nucleophilic attack of the nitrogen of the amino group in 2 at the carbonyl carbon of 1 would lead to intermediate A which on reaction with 1 would give cyclic intermediate B. Hydrolysis of B would give 3 and hydrazinylphosphonic acid as a side product.

The utility of 3 in organic synthesis has been tested on reactions with nucleophiles. Reactions of 3c,d and thiophenol, sodium phenylsulfinate, hydroxylamine hydrochloride and piperidine in boiling ethanol afforded the corresponding azines 5–8 (Scheme 3) in good yields. The reactions proceeded via replacement of the two chlorine atoms in compounds 3c,d. Similar related reactions have been reported.^[33–35] The X-ray crystal structure of compound 5b is shown in Figure 3.

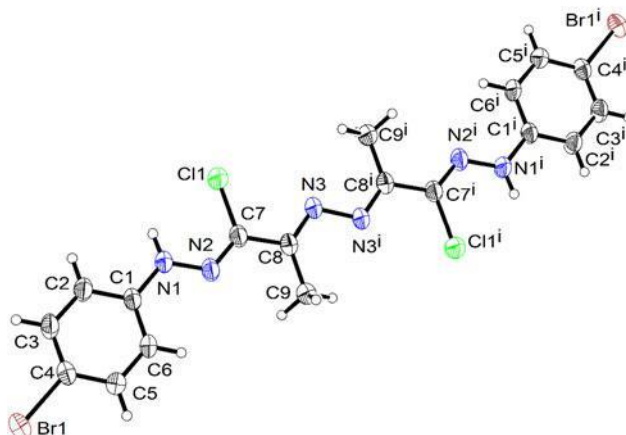


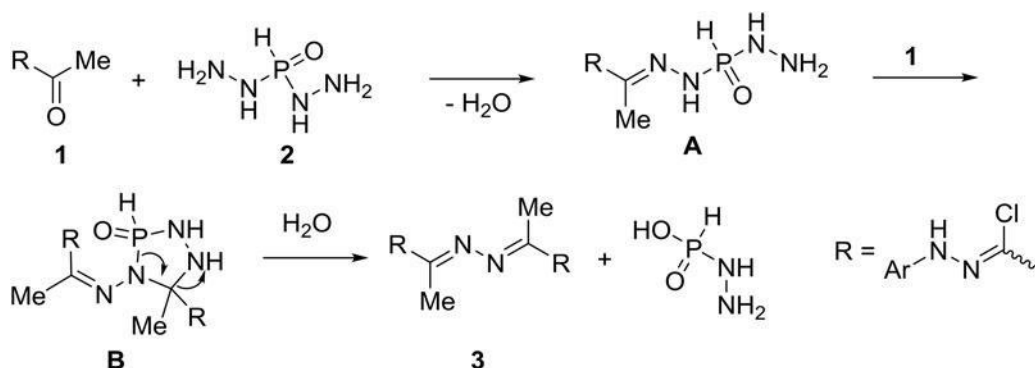
Figure 2. Ortep representation of the molecular structure 3d showing 50% probability ellipsoids.

Reaction of methyl ketones 9 and 2 in boiling ethanol for 2–3 h furnished the corresponding azines 10a–e (Scheme 4) in good yields. The structures of 10a and 10b were confirmed by X-ray crystallography as shown in Figures 4 and 5, respectively. The spectral data for 10a,b were in agreement with those reported.^[36,37]

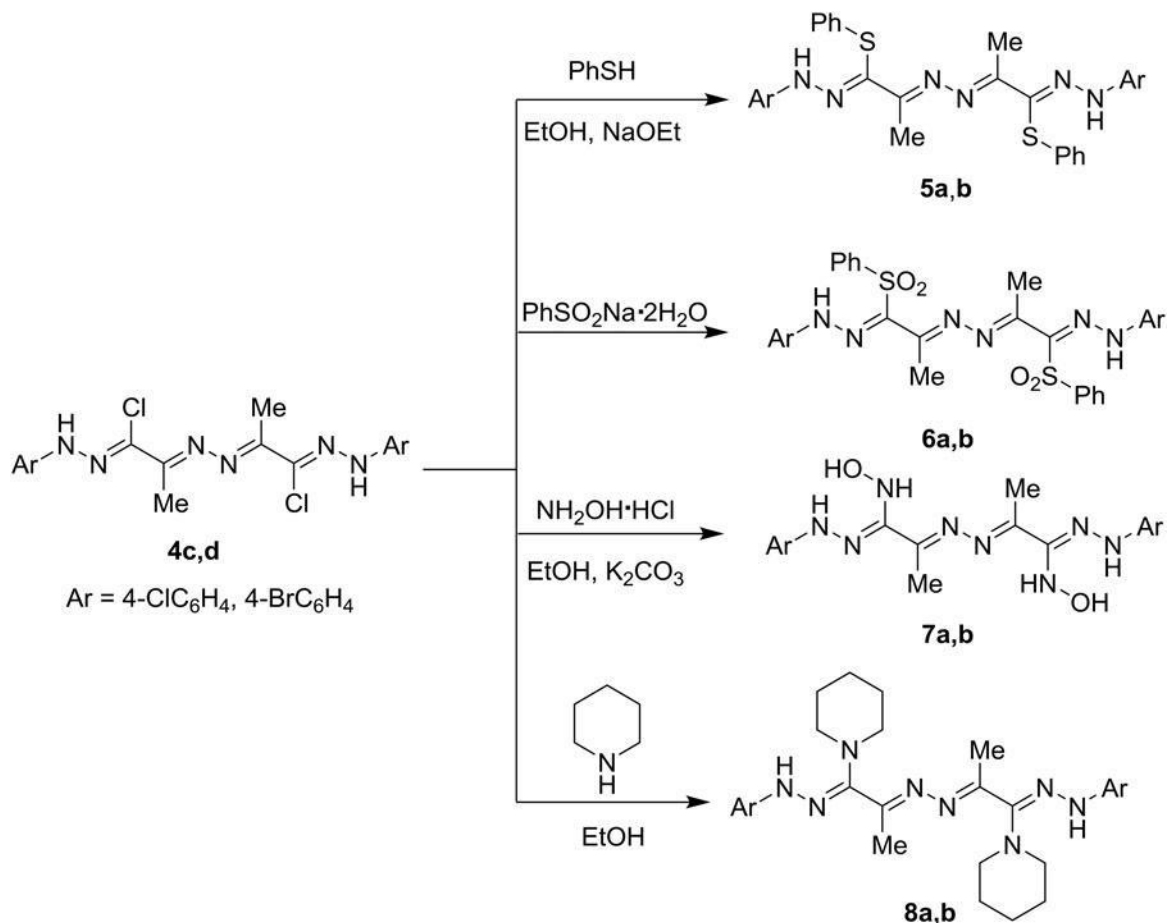
Similarly, reaction of isatin (11) and 2 in ethanol under reflux for 3 h afforded (3*Z*,3'*E*)-3,3'-(hydrazine-1,2-diylidene)bis(indolin-2-one) (12) in 85% yield (Scheme 5). The X-ray crystal structure of 12 is shown in Figure 6. The spectral data for 12 were in agreement with those reported.^[38] For example, the IR spectrum showed a strong absorption peak at 1725 cm⁻¹ which is attributed to the carbonyl group. The carbonyl carbon appeared at 164.1 ppm in the ¹³C NMR spectrum. In addition, the ¹H NMR spectrum showed the presence of exchangeable singlets that appeared at 10.61 ppm due to the two NH protons.

Discussion of molecular structures

Data refinement parameter, bond lengths and angles obtained by single crystal diffraction are shown in Tables S1–S12. The molecule of 3c has inversion symmetry and, apart from the methyl hydrogen atoms, is planar with a maximum deviation of 0.11(1) Å from the least squares plane through the atoms (Figure 1). The molecule of 3d also has inversion symmetry and is planar apart from the methyl hydrogen atoms with a maximum deviation of 0.11(1) Å from the least squares plane (Figure 2). The molecule of 5b has inversion symmetry and,



Scheme 2. Possible pathway for the formation of azines 3.



Scheme 3. Synthesis of azines 5–8.

with the exception of the phenyl group and methyl hydrogen atoms, is planar with a maximum deviation of 0.105(2) Å from the least squares plane (Figure 3).

In 10a, the separate dihydrobenzofuranyl ethanimine fragments of the molecule are planar (apart from the methyl hydrogen atoms) with a maximum deviation of 0.192(2) Å from their least squares planes (Figure 4). The twist angle between the two fragments of the molecule is 55.66(3)°. For 10b, the molecule has pseudo-inversion symmetry in the crystal (Figure 5). In contrast to 10a, the molecule is essentially planar with a maximum deviation of 0.268(2) Å from the least squares plane of the molecule (apart from the methyl hydrogen atoms). Molecule 12 has inversion symmetry and is planar with a maximum deviation of ± 0.0706

(14) from the least squares plane through the atoms (Figure 6).

The planar geometry and inversion symmetry generally observed for these materials (except for 10a) is akin to that observed for 3,3⁰-(hydrazine-1,2-diylidenedieth-1-yl-1-ylidene)bis(1H-pyrazole).^[39]

Experimental

General

Melting points were recorded on a Gallenkamp melting point apparatus. The IR spectra (KBr disks) were obtained using PerkinElmer GX Spectrometer. The NMR spectra

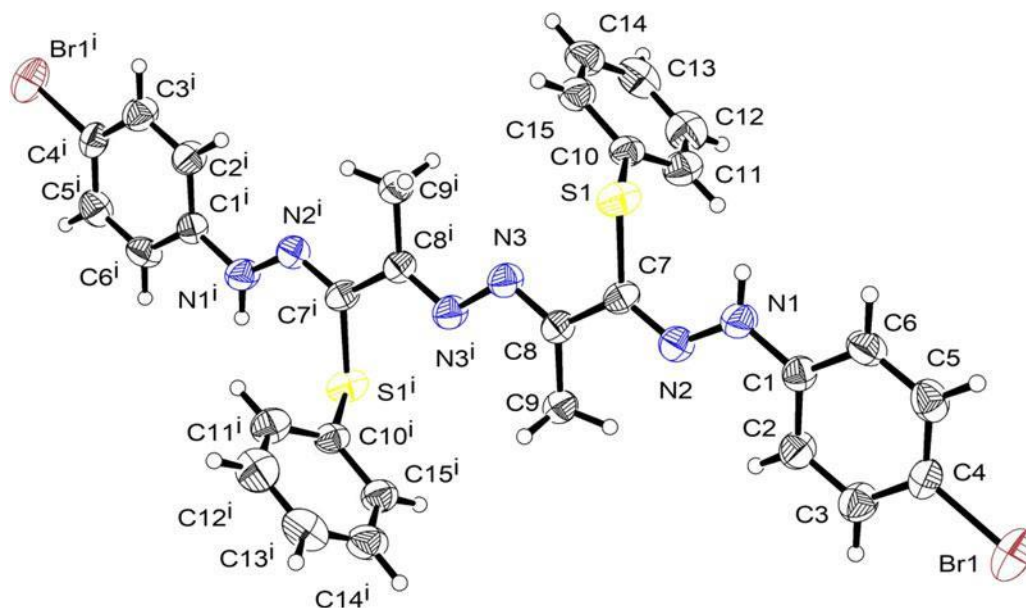
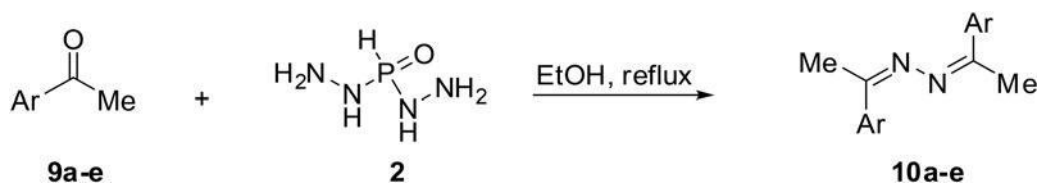


Figure 3. Ortep representation of the molecular structure of 5b showing 50% probability ellipsoids.



Scheme 4. Synthesis of azines 10a-e.

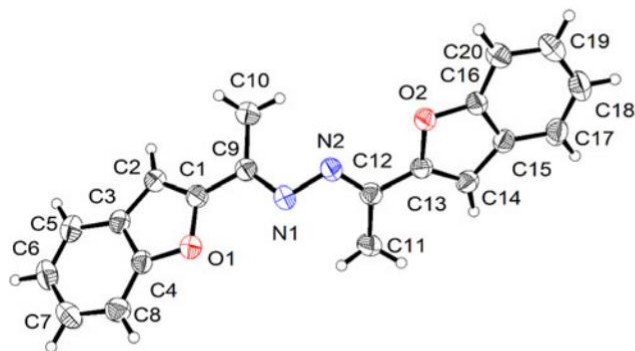


Figure 4. Ortep representation of the molecular structure of 10a showing 50% probability ellipsoids.

were carried out on JEOL 500 MHz spectrometer (TMS; δ in ppm and J in Hz) at 500 MHz for ^1H and 125 MHz for ^{13}C NMR, in DMSO- d_6 unless otherwise indicated. The crystallographic data for compounds 3c, 3d, 5b, 10a, 10b, and 12 were deposited at the Cambridge Crystallographic Data Center with CCDC reference numbers 1861134–1861139. Phosphonic dihydrazide 2 was produced based on a literature procedure.^[40] The [Supplemental Materials](#) contains sample ^1H and ^{13}C NMR spectra for products 3, 5, and 6 (Figures S1 – S11).

Synthesis of 3a–e: A mixture of **1** (10.0 mmol) and **2** (0.55 g, 5.0 mmol) in EtOH (20 mL) was refluxed for 3 h. The solid formed on cooling was filtered and recrystallized from EtOH to give pure **3**.

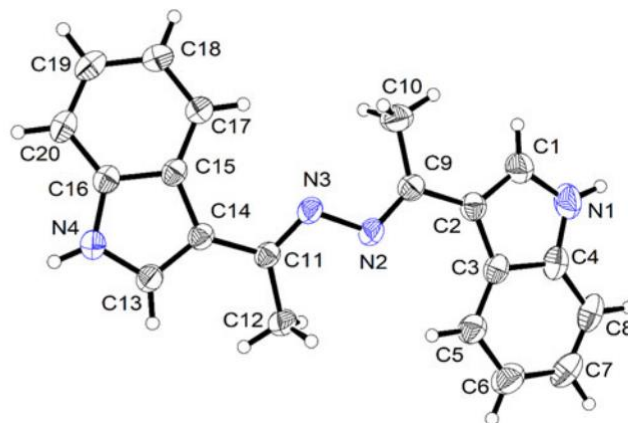
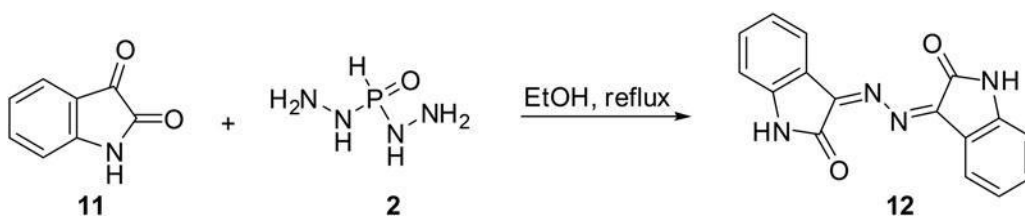


Figure 5. Ortep representation of the molecular structure of 10b showing 50% probability ellipsoids.

(1*Z*,1'*Z*,2*E*,2'*E*)-2,2'-bis(1,2-dihydrazinylidene)bis(*N*⁰-phenylpropanehydrazonoyl chloride) (**3a**): m.p., 197–198 °C, brown, yield, 85%; IR (ν_{max} , cm^{-1}): 3319 (NH), 1602 (C $\frac{1}{4}$ N), 1541, 1508 (C $\frac{1}{4}$ C). ^1H NMR (δ_{H} , ppm): 2.25 (s, 6 H, 2Me), 6.93 (t, J $\frac{1}{4}$ 8.5 Hz, 2 H, H-4 of 2Ph), 7.30 (t, J $\frac{1}{4}$ 8.5 Hz, 4 H, H-3/H-5 of 2Ph), 7.36 (d, 4 H, ^{13}J $\frac{1}{4}$ 8.5 Hz, H-2/H-6 of 2Ph), 10.32 (s, exch., 2 H, 2NH). ^{13}C NMR (δ_{C} , ppm): 14.6 (Me), 114.0, 123.2, 129.2, 143.4, 153.9 (C-Cl), 155.7 (C-Me). Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{Cl}_2\text{N}_6$ (389.28): C, 55.54; H, 4.66; N, 21.59, Found: C, 55.21; H, 4.42; N, 21.44%.



Scheme 5. Synthesis of (3Z,3'E)-3,3'-(hydrazine-1,2-diylidene)bis(indolin-2-one) (12).

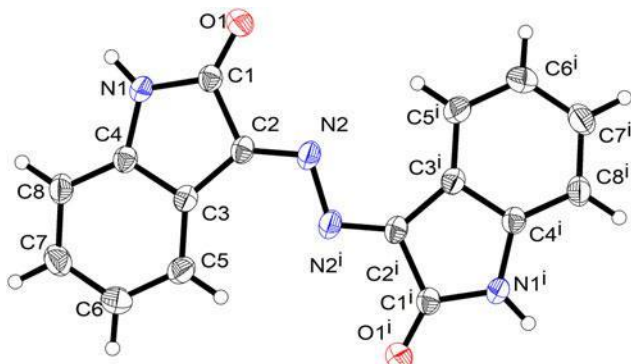


Figure 6. Ortep representation of the molecular structure of 12 showing 50% probability ellipsoids.

(1Z,1⁰Z,2E,2⁰E)-2,2⁰-(Hydrazine-1,2-diylidene)bis(N-(4-fluorophenyl)propanehydrazonoyl chloride) (3b): m.p., 193–194 °C, red, yield, 89%; IR (max, cm⁻¹): 3329 (NH), 1600 (C ¼ N), 1541, 1510 (C ¼ C). ¹H NMR (d_H, ppm): 2.24 (s, 6 H, 2Me), 7.34 (d, 4 H, J ¼ 8.4 Hz, H-2/H-6 of 2Ar), 7.37 (d, ⁴₁₃ J ¼ 8.4 Hz, H-3/H-5 of 2Ar), 10.34 (s, exch., 2 H, 2NH). ¹³C NMR (d_C, ppm): 14.6 (Me), 114.3, 116.5, 131.8, 143.4, 153.9 (C-Cl), 156.4 (C-Me). Anal. Calcd. for C₁₈H₁₆Cl₂F₂N₆ (425.26): C, 50.84; H, 3.79; N, 19.76, Found: C, 50.59; H, 3.57; N, 19.63%.

(1Z,1⁰Z,2E,2⁰E)-2,2⁰-(Hydrazine-1,2-diylidene)bis(N⁰-(4-chlorophenyl)propanehydrazonoyl chloride) (3c): m.p., 217–218 °C, brown, yield, 90%; IR (max, cm⁻¹): 3325 (NH), 1595 (C ¼ N), 1552, 1500 (C ¼ C). ¹H NMR (d_H, ppm): 2.26 (s, 6 H, 2Me), 7.30 (d, 4 H, J ¼ 8.1 Hz, H-2/H-6 of 2Ar), 7.37 (d, 4 H, J ¼ 8.1 Hz, H-3/H-5 of 2Ar), 10.45 (s, exch., 2 H, 2NH). ¹³C NMR (d_C, ppm): 14.6 (Me), 115.0, 123.5, 129.8, 142.2, 153.4 (C-Cl), 155.9 (C-Me); Anal. Calcd. for C₁₈H₁₆Cl₄N₆ (458.17): C, 47.19; H, 3.52; N, 18.34, Found: C, 46.97; H, 3.35; N, 18.19%.

(1Z,1⁰Z,2E,2⁰E)-2,2⁰-(Hydrazine-1,2-diylidene)bis(N⁰-(4-bromophenyl)propanehydrazonoyl chloride) (3d): m.p., 227–228 °C, brown, yield, 87%; IR (max, cm⁻¹): 3325 (NH), 1591 (C ¼ N), 1552 s, 1497 s (C ¼ C); ¹H NMR (d_H, ppm): 2.21 (s, 6 H, 2Me), 7.36 (d, 4 H, J ¼ 8.0 Hz, H-2/H-6 of 2Ar), 7.63 (d, 4 H, ¹³J ¼ 8.0 Hz, H-3/H-5 of 2Ar), 10.43 (s, exch., 2 H, 2NH); ¹³C NMR (d_C, ppm): 14.6 (Me), 115.0, 116.0, 132.5, 143.2, 153.4 (C-Cl), 156.0 (C-Me); Anal. Calcd. for C₁₈H₁₆Br₂Cl₂N₆ (547.08): C, 39.52; H, 2.95; N, 15.36, Found: C, 39.37; H, 2.79; N, 15.18%.

(1Z,1⁰Z,2E,2⁰E)-2,2⁰-(Hydrazine-1,2-diylidene)bis(N⁰-(4-iodophenyl)propanehydrazonoyl chloride) (3e): m.p., 230–231 °C, red, yield, 80%; IR (max, cm⁻¹): 3323 (NH), 1590 (C ¼ N), 1552, 1496 (C ¼ C). ¹H NMR (d_H, ppm): 2.19 (s, 6 H, 2Me), 7.28 (d, 4 H, J ¼ 7.9 Hz, H-2/H-6 of 2Ar), 7.67

(d, 4 H, J ¼ 7.9 Hz, H-3/H-5 of 2Ar), 10.47 (s, exch., 2 H, 2NH). ¹³C NMR (d_C, ppm): 14.6 (Me), 87.0, 116.0, 135.6, 143.2, 154.0 (C-Cl), 156.5 (C-Me). Anal. Calcd. for C₁₈H₁₆Cl₂I₂N₆ (641.08): C, 33.72; H, 2.52; N, 13.11, Found: C, 33.64; H, 2.43; N, 13.02%.

Synthesis of 5a,b: A mixture of thiophenol (0.22 g, 2.0 mmol) and 3c or 3d (1.0 mmol) was added to dry EtOH (30 mL) containing sodium (46 mg, 2.0 mmol). The mixture was refluxed for 6 h and the solid formed on cooling was isolated by filtration, washed with EtOH, dried and recrystallized from EtOH to give 5a or 5b, respectively.

(1Z,1⁰Z,2E,2⁰E)-Diphenyl 2,2⁰-(hydrazine-1,2-diylidene)bis(N⁰-4-chlorophenylpropanehydrazono-thioate) (5a): m.p., 158–159 °C, red, yield, 85%; IR (max, cm⁻¹): 3270 (NH), 1590, 1578 (C ¼ N), 1510, 1475 (C ¼ C). ¹H NMR (d_H, ppm): 1.82 (s, 6 H, 2Me), 7.32–7.37 (m, 18 H, 2Ph and 2Ar), 10.6 (s, exch., 2 H, 2NH). ¹³C NMR (d_C, ppm): 13.87 (Me), 112.7, 116.2, 126.0, 127.5, 129.3, 131.7, 133.9, 135.8, 142.8 (C-S), 155.2 (C-Me). Anal. Calcd. for C₃₀H₂₆Cl₂N₆S₂ (605.60): C, 59.50; H, 4.33; N, 13.88, Found: C, 59.32; H, 4.15; N, 13.67%.

(1Z,1⁰Z,2E,2⁰E)-Diphenyl 2,2⁰-(hydrazine-1,2-diylidene)bis(N⁰-4-bromophenylpropanehydrazono-thioate) (5b): m.p., 160–161 °C, red, yield, 86%; IR (max, cm⁻¹): 3269 (NH), 1591, 1575 (C ¼ N), 1510, 1475 (C ¼ C). ¹H NMR (d_H, ppm): 1.82 (s, 6 H, 2Me), 7.17–7.28 (m, 10 H, 2Ph), 7.37 (d, 4 H, J ¼ 8.0 Hz, H-2/H-6 of 2Ar), 7.51 (d, ⁴₁₃ J ¼ 8.0 Hz, H-3/H-5 of 2Ar), 10.60 (s, exch., 2 H, 2NH). ¹³C NMR (d_C, ppm): 13.9 (Me), 112.7, 116.2, 126.0, 127.5, 129.3, 131.7, 133.9, 135.8, 142.8 (C-S), 155.2 (C-Me). Anal. Calcd. for C₃₀H₂₆Br₂N₆S₂ (694.51): C, 51.88; H, 3.77; N, 12.10, Found: C, 51.67; H, 3.62; N, 11.92%.

Synthesis of 6a,b: A mixture of 3c or 3d (1.0 mmol) and sodium benzenesulfinate dihydrate (0.80 g, 4.0 mmol) in EtOH (30 mL) was heated under reflux for 2 h. The solid produced on cooling was filtered, washed with EtOH, dried and recrystallized from EtOH to give 6a or 6b, respectively.

(1E,2E)-1,2-bis((Z)-1-(2-(4-Chlorophenyl)hydrazono)-1-(phenylsulfonyl)propan-2-ylidene)hydrazine (6a): m.p., 219–220 °C, brown, yield, 89%; IR (max, cm⁻¹): 3325 (NH), 1597 (C ¼ N), 1552, 1500 (C ¼ C). ¹H NMR (d_H, ppm): 2.22 (s, 6 H, 2Me), 7.32–7.37 (m, 18 H, 2Ph and 2Ar), 10.45 (s, exch. 2 H, 2NH). ¹³C NMR (d_C, ppm): 14.6 (Me), 115.5, 116.2, 124.0, 125.0, 129.0, 142.4, 145.8 (C-S), 153.2 (C-Me). Anal. Calcd. for C₃₀H₂₆Cl₂N₆O₄S₂ (669.60): C, 53.81; H, 3.91; N, 12.55, Found: C, 53.69; H, 3.78; N, 12.39%.

(1E,2E)-1,2-bis((Z)-1-(2-(4-Bromophenyl)hydrazono)-1-(phenylsulfonyl)propan-2-ylidene)hydrazine (6b): m.p., 252–253 °C, brown, yield, 90%; IR (max, cm⁻¹): 3325 (NH), 1591 (C ¼ N), 1552, 1496 (C ¼ C). ¹H NMR (d_H, ppm): 1.87

(s, 6 H, 2Me), 7.27–7.32 (m, 10 H, 2Ph), 7.39 (d, 4 H, J $\frac{1}{4}$ 8.0 Hz, H-2/H-6 of 2Ar), 7.55 (d, 4 H, J $\frac{1}{4}$ 8.0 Hz, H-3/H-5 of 2Ar), 10.63 (s, exch., 2 H, 2NH). ^{13}C NMR (d_C, ppm): 13.9 (CH₃), 112.7, 116.2, 126.0, 127.5, 129.3, 131.7, 133.9, 137.8, 142.8 (C-S), 155.9 (C-Me). Anal. Calcd. for C₃₀H₂₆Br₂N₆O₄S₂ (758.50): C, 47.50; H, 3.46; N, 11.08, Found: C, 47.36; H, 3.29; N, 10.89%.

Synthesis of 7a,b: Hydroxylamine hydrochloride (0.14 g, 2.0 mmol) and anhydrous potassium carbonate (0.28 g, 2.1 mmol) was added to a solution of 3c or 3d (1.0 mmol) in dry EtOH (30 mL). The mixture was refluxed for 3 h and the solid formed on cooling was filtered and recrystallized from EtOH to give 7a or 7b, respectively.

(1Z,1⁰Z,2E,2⁰E)-2,2⁰-(Hydrazine-1,2-diylidene)bis(N⁰-(4-chlorophenyl)-N-hydroxypropane-hydrazoneamide) (7a): m.p., 235–236 °C, red, yield, 83%; IR (max, cm⁻¹): 3392 (OH), 3244 (NH), 1597 (C $\frac{1}{4}$ N), 1496 (C $\frac{1}{4}$ C). ^1H NMR (d_H, ppm): 2.22 (s, 6 H, 2Me), 7.18 (d, 4 H, J $\frac{1}{4}$ 8.0 Hz, H-2/H-6 of 2Ar), 7.32 (d, 4 H, J $\frac{1}{4}$ 8 Hz, H-3/H-5 of 2Ar), 7.70 (s, exch., 2 H, 2OH), 7.80 (s, exch., 2 H, 2NH), 10.46 (s, exch., 2 H, 2NH). ^{13}C NMR (d_C, ppm): 13.9 (Me), 113.6, 116.0, 126.0, 131.9, 143.8 (C-NH), 152.7 (C-Me). Anal. Calcd. for C₁₈H₂₀Cl₂N₈O₂ (451.31): C, 47.90; H, 4.47; N, 24.83, Found: C, 47.76; H, 4.31; N, 24.67%.

(1Z,1⁰Z,2E,2⁰E)-2,2⁰-(Hydrazine-1,2-diylidene)bis(N⁰-(4-bromophenyl)-N-hydroxypropane-hydrazoneamide) (7b): m.p., 254–255 °C, brown, yield, 87%; IR (max, cm⁻¹): 3400 (OH), 3325 (NH), 1591 (C $\frac{1}{4}$ N), 1552, 1500 (C $\frac{1}{4}$ C). ^1H NMR (d_H, ppm): 2.22 (s, 6 H, 2Me), 7.30 (d, 4 H, J $\frac{1}{4}$ 9.0 Hz, H-2/H-6 of 2Ar), 7.45 (d, 4 H, J $\frac{1}{4}$ 9.0 Hz, H-3/H-5 of 2Ar), 7.70 (s, exch., 2 H, 2OH), 7.90 (s, exch., 2 H, 2NH), 10.46 (s, exch., 2 H, 2NH). ^{13}C NMR (d_C, ppm): 14.6 (Me), 112.8, 116.0, 124.0, 131.9, 142.7 (C-NH), 153.7 (C-Me). Anal. Calcd. for C₁₈H₂₀Br₂N₈O₂ (540.22): C, 40.02; H, 3.73; N, 20.74, Found: C, 39.92; H, 3.61; N, 20.56%.

Synthesis of 8a,b: A mixture of 3c or 3d (1.0 mmol) in dry EtOH (30 mL) containing piperidine (0.34 g, 4.0 mmol) was then refluxed for 6 h. The solid formed on cooling was filtered and recrystallized from EtOH to yield 8a or 8b, respectively.

(1E,2E)-1,2-bis((Z)-1-(2-(4-Chlorophenyl)hydrazono)-1-(piperidin-1-yl)propan-2-ylidene)hydrazine (8a): m.p., 228–229 °C, red, yield, 82%; IR (max, cm⁻¹): 3310 (NH), 1601 (C $\frac{1}{4}$ N), 1562, 1510 (C $\frac{1}{4}$ C). ^1H NMR (d_H, ppm): 1.58–1.62 (m, 12 H, H-3/H-4/H-5 of 2 piperidiny), 2.26 (s, 6 H, 2Me), 3.16 (m, 8 H, H-2/H-6 of 2 piperidiny), 7.28 (d, 4 H, J $\frac{1}{4}$ 8 Hz, H-2/H-6 of 2Ar), 7.36 (d, 4 H, J $\frac{1}{4}$ 8 Hz, H-3/H-5 of 2Ar), 10.45 (s, exch., 2 H, 2NH). ^{13}C NMR (d_C, ppm): 14.6 (Me), 23.7 (C-4 of piperidiny), 25.3 (C-3/C-5 of piperidiny), 48.7 (C-2/C-6 of piperidiny), 115.0, 124.5, 129.8, 142.21, 153.4 (C-piperidiny), 155.8 (C-Me). Anal. Calcd. for C₂₈H₃₆Cl₂N₈ (555.55): C, 60.54; H, 6.53; N, 20.17, Found: C, 60.36; H, 6.33; N, 20.02%.

(1E,2E)-1,2-bis((Z)-1-(2-(4-Bromophenyl)hydrazono)-1-(piperidin-1-yl)propan-2-ylidene)hydrazine (8b): m.p., 236–237 °C, red, yield, 80%; IR (max, cm⁻¹): 3295 (NH), 1597 (C $\frac{1}{4}$ N), 1560, 1490 (C $\frac{1}{4}$ C). ^1H NMR (d_H, ppm): 1.57–1.63 (m, 12 H, H-3/H-4/H-5 of 2 piperidiny), 2.26 (s, 6 H, 2Me), 3.16 (m, 8 H, H-2/H-6 of 2 piperidiny), 7.35 (d,

4 H, J $\frac{1}{4}$ 8 Hz, H-2/H-6 of 2Ar), 7.476 (d, 4 H, J $\frac{1}{4}$ 8.5 Hz, H-3/H-5 of 2Ar), 10.55 (s, exch., 2 H, 2NH). ^{13}C NMR (d_C, ppm): 14.6 (Me), 23.0 (C-4 of piperidiny), 25.5 (C-3/C-5 of piperidiny), 48.7 (C-2/C-6 of piperidiny), 116.0, 117.0, 131.8, 142.2, 153.4 (C-piperidiny), 154.7 (C-Me). Anal. Calcd. for C₂₈H₃₆Br₂N₈ (644.46): C, 52.18; H, 5.63; N, 17.39, Found: C, 52.01; H, 5.45; N, 17.21%.

Synthesis of 10a–e: A mixture of ketones 9 (20 mmol) and 2 (1.10 g, 10 mmol) in EtOH (20 mL) was refluxed for 2–3 h. The solid produced on cooling was filtered, dried and recrystallized from EtOH to give 10.

(1Z,2Z)-1,2-bis(1-(Benzofuran-2-yl)ethylidene)hydrazine (10a): m.p., 163–165 °C (lit. m.p. 163–164 °C^[36]), red, yield, 88%. The spectral data for 10a was in agreement with those reported.^[36]

(1Z,2Z)-1,2-bis(1-(1H-Indol-3-yl)ethylidene)hydrazine (10b): m.p., 280–281 °C (lit. m.p. 280–282 °C^[37]), red, yield, 80%. The spectral data for 10b was in agreement with those reported.^[37]

(1Z,2Z)-1,2-bis(1-(5-Methyl-1-phenyl-1H-1,2,3-triazol-4-yl)ethylidene)hydrazine (10c): m.p., 260–261 °C, yellow, yield, 82%; IR (max, cm⁻¹): 1614, 1598 (C $\frac{1}{4}$ N), 1500 (C $\frac{1}{4}$ C). ^1H NMR (CDCl₃; d_H, ppm): 2.47 (s, 6H, 2Me), 2.70 (s, 6 H, 2Me), 7.25–7.30 (m, 10 H, 2Ph). ^{13}C NMR (CDCl₃; d_C, ppm): 10.5 (Me), 21.34 (Me), 115.0, 125.0, 131.1, 133.1, 139.6, 144.4, 160.0 (C-Me). Anal. Calcd. for C₂₂H₂₂N₈ (398.47): C, 66.31; H, 5.57; N, 28.12, Found: C, 66.13; H, 5.39; N, 27.98%.

(1Z,2Z)-1,2-bis(1-(1-(4-Fluorophenyl)-5-methyl-1H-1,2,3-triazol-4-yl)ethylidene)hydrazine (10d): m.p., >300 °C, pale yellow, yield, 81%; IR (max, cm⁻¹): 1614 (C $\frac{1}{4}$ N), 1514 (C $\frac{1}{4}$ C). ^1H NMR (CDCl₃; d_H, ppm): 2.47 (s, 6 H, 2Me), 2.70 (s, 6 H, 2Me), 7.35 (d, 4 H, J $\frac{1}{4}$ 8 Hz, H-2/H-6 of 2Ar), 7.38 (d, 4 H, J $\frac{1}{4}$ 8 Hz, H-3/H-5 of 2Ar). ^{13}C NMR (CDCl₃; d_C, ppm): 10.8 (Me), 21.3 (Me), 116.0, 124.7, 132.5, 135.3, 141.5, 145.2, 161.2 (C-Me). Anal. Calcd. for C₂₂H₂₀F₂N₈ (434.45): C, 60.82; H, 4.64; N, 25.79, Found: C, 60.67; H, 4.51; N, 25.57%.

(1Z,2Z)-1,2-bis(1-(5-Methyl-1-(4-tolyl)-1H-1,2,3-triazol-4-yl)ethylidene)hydrazine (10e): m.p., 285–286 °C, yellow, yield, 86%; IR (max, cm⁻¹): 1612 (C $\frac{1}{4}$ N), 1552, 1520 (C $\frac{1}{4}$ C). ^1H NMR (CDCl₃; d_H, ppm): 2.47 (s, 6 H, 2Me), 2.68 (s, 6 H, 2Me), 2.75 (s, 6 H, 2Me), 7.26–7.39 (m, 8 H, 2Ar). ^{13}C NMR (CDCl₃; d_C, ppm): 11.5 (Me), 21.3 (Me), 27.9 (Me), 125.0, 125.2, 130.14, 130.2, 140.4, 144.0, 157.0 (C-Me). Anal. Calcd. for C₂₄H₂₆N₈ (426.53): C, 67.58; H, 6.14; N, 26.27, Found: C, 67.45; H, 5.97; N, 26.07%.

Synthesis of (3Z,3⁰E)-3,3⁰-(hydrazine-1,2-diylidene)diindolin-2-one (12): A mixture of 11 (1.47 g, 10 mmol) and 2 (0.55 g, 5 mmol) in EtOH (20 mL) was refluxed for 3 h. The solid obtained on cooling was filtered, dried and recrystallized from EtOH to give 12 as red crystals, yield 2.58 g (89%), m.p. 293–294 °C (lit. m.p. > 300 °C^[38]). The spectral data was in agreement with those reported.

Crystal structure determination

Single-crystal XRD data were collected on an Agilent SuperNova Dual Atlas diffractometer with a mirror

monochromator using either Cu ($k\frac{1}{4}$ 1.5418 Å) or Mo ($k\frac{1}{4}$ 0.7107 Å) radiation. Crystal structures were solved using SHELXS^[41] and refined using SHELXL.^[42] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were inserted in idealized positions, and a riding model was used with $U_{iso}(H)$ set at 1.2 or 1.5 times the value of $U_{eq}(C/N)$. Data collection and refinement parameters are shown in Tables S1–S12 (Supplemental Materials).

Conclusions

New, simple and efficient procedures have been developed for the synthesis of symmetrical azines in high yields from phosphonic dihydrazide and commercially available reagents.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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